32

FLUORESCENCE SPECTRA OF SOME URANYL SALTS

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Plate IV (A and B) Plate V (A and B)

ABSTRACT. The fluorescence spectra of uranyl acetate, nitrate, sulphate, fluoride I, chloride, potassium uranyl sulphate and ammonium uranyl sulphate have been reinvestigated at room and liquid air temperatures and new analyses have been proposed for each spectrum on the basis of a single electronic allowed transition.

INTRODUCTION

The fluorescence spectra of uranyl compounds are studied in detail by many workers since the first investigations were made by Becquerel (1872) and Becquerel and Onnes (1909). In our earlier paper (Rao and Narasimham, 1956), a comprehensive review of the available literature on the spectroscopic properties of the uranyl salts was given. It was shown that the earlier analyses of Freymann (1946) and Pant (1945, 1950) were open to question in several respects. The most satisfactory analysis of the compounds has been proposed by Dieke and Duncan (1949) but they gave analysis for the spectra of only two salts—caesium uranyl nitrate and caesium uranyl chloride. Therefore investigations are again carried out on uranyl acetate ($2H_2O$), nitrate ($6H_2O$), sulphate ($3H_2O$), chloride ($1H_2O$), fluoride I (XH_2O), potassium sulphate ($2H_2O$) and ammonium sulphate ($2H_2O$) at room and liquid air temperatures and new analyses have been proposed for the fluorescence bands of each compound on the basis of a single electronic transition with one upper state and one lower state. In the case of ammonium uranyl sulphate, the analysis of the fluorescence bands has been proposed for the first time.

EXPERIMENTAL

The experimental set-up for fluorescence consists of a brass rod with a circular slot of 5 cm. depth in the middle in which a small glass tube containing the investigating salt in fine powder form is placed tightly. The brass rod has three small holes bored at the middle of the slot (2.5 cm. from the top) two in one line to allow the incident light on the substance from two mercury arcs on opposite sides and the third perpendicular to the line joining the above two. This allows the fluorescence from the substance into the spectrograph.

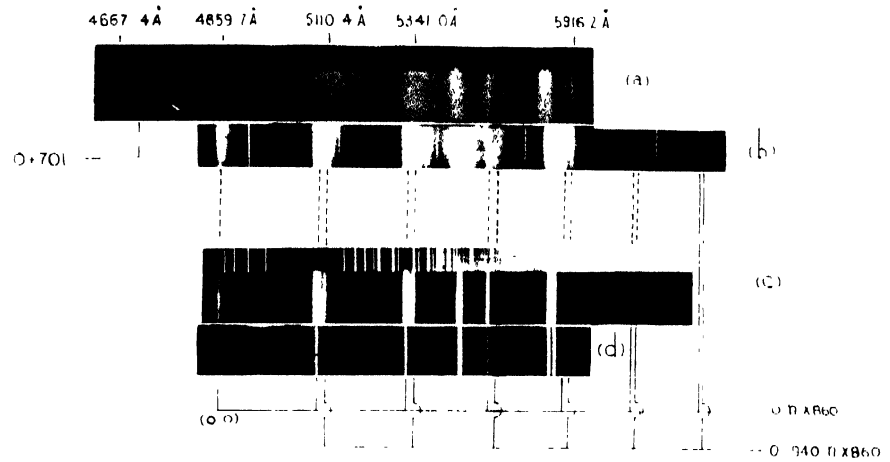

Fig. 1. Fluorescence spectra of uranyl acetate

(a) At room temperature.
(b) At liquid air temperature (exposure 1 hour).
(c) At liquid air temperature (exposure 20 minutes).
(d) At liquid air temperature (exposure 5 minutes).

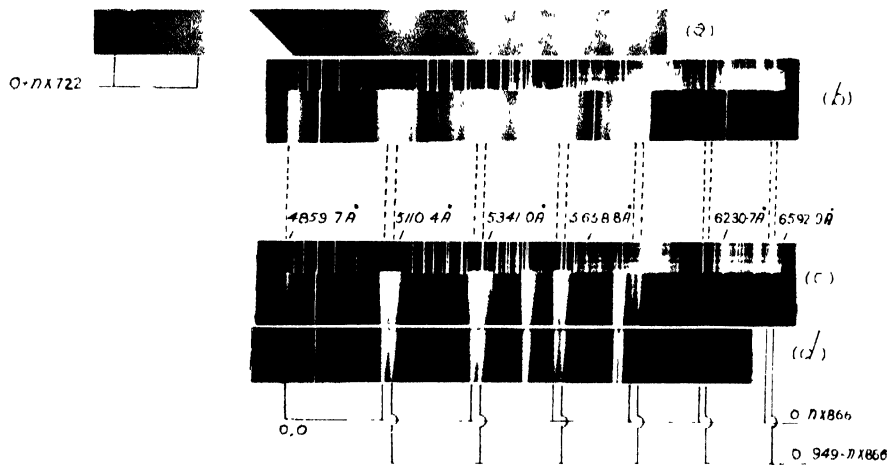

Fig. 2. Fluorescence spectra of uranyl nitrate

(a) At room temperature.
(b) At liquid air temperature (exposure 1 hour).
(c) At liquid air temperature (exposure 20 minutes).
(d) At liquid air temperature (exposure 5 minutes).

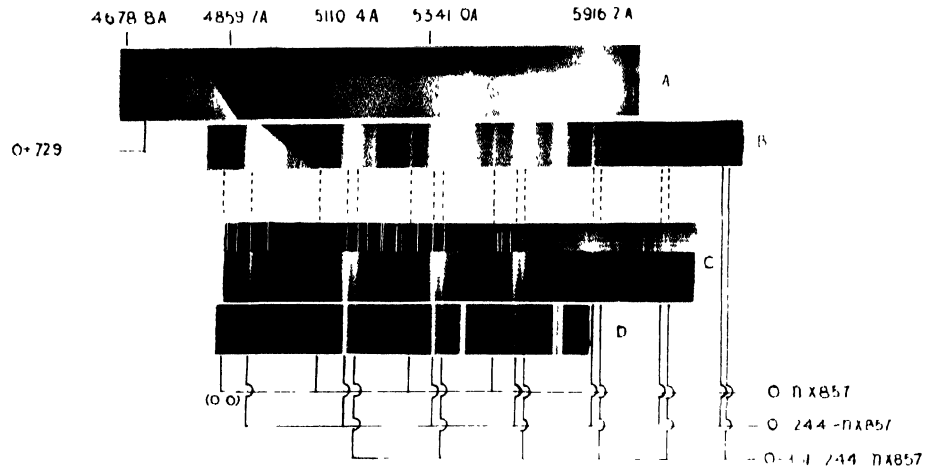

Fig. 3. Fluorescence spectra of uranyl sulphate

(a) At room temperature.
(b) At liquid air temperature (exposure 1 hour).
(c) At liquid air temperature (exposure 20 minutes).
(d) At liquid air temperature (exposure 5 minutes).

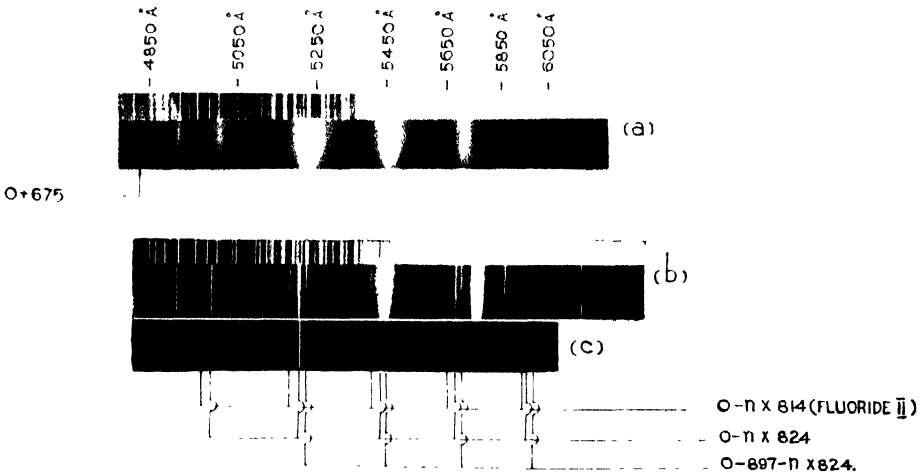

Fig. 4. Fluorescence spectra of uranyl fluoride I

(a) At room temperature.
(b) At liquid air temperature (long exposure).
(c) At liquid air temperature (short exposure).

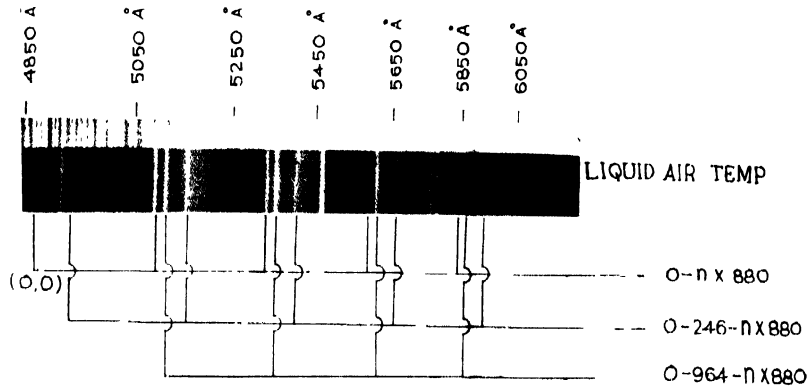

Fig. 5. Fluorescence spectrum of uranyl chloride

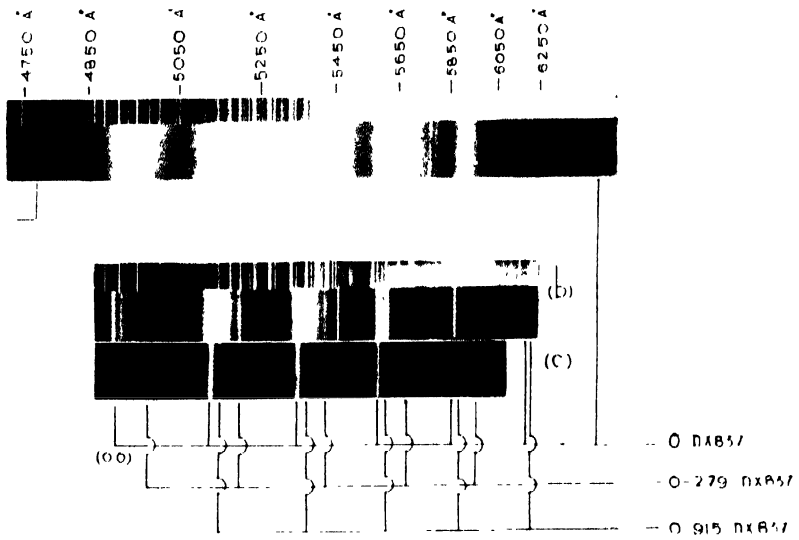

Fig. 6. Fluorescence spectra of potassium uranyl sulphate

(a) At room temperature.
(b) At liquid air temperature (long exposure).
(c) At liquid air temperature (short exposure).

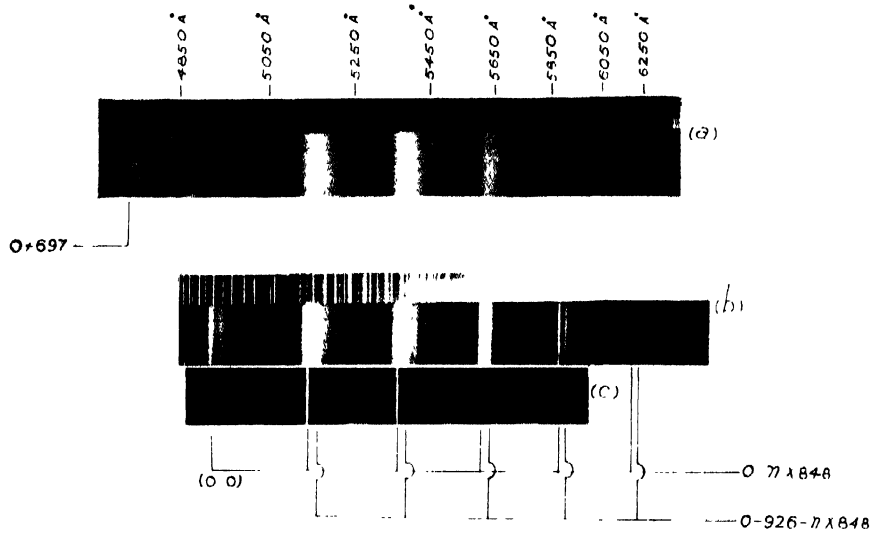

Fig. 7. Fluorescence spectra of ammonium uranyl sulphate

(a) At room temperature.

(b) At liquid air temperature (long exposure)

(c) At liquid air temperature (short exposure).

A special type of quartz Dewar flask (supplied by Thermal Syndicate Ltd.) is used as the container for the liquid air to study the fluorescence spectra at liquid air temperature. The Dewar flask has three fused plane windows on each wall. The holes in the brass rod could be alligned parallel to these windows. The brass rod is suspended by means of a wire into the liquid air contained in the Dewar flask. The specimen under investigation was found to acquire a temperature of −177°C. The spectrum is photographed on a Fuess spectrograph (dispersion of 33 Å/mm at λ5000 Å) using Ilford HP3 panchromatic plates.

With this set-up, exposures are given ranging from a few minutes to one hour. A very intense picture with even the weakest bands can be obtained in one hour exposure while five minute's exposure is sufficient to bring out the principal bands of the spectrum.

The fluorescence spectra are taken at liquid air and room temperatures. In all cases, mercury arcs are used as sources of exciting radiations and glass filters having a low transmission value from the blue green to higher wavelengths are used to eliminate the mercury lines in the fluorescence region. The bands are measured against standard iron arc lines. The accuracy of measurements for the sharp bands is 2 cm^{-1}, 5 cm^{-1} for moderate diffuse bands and 15 cm^{-1} for very diffuse bands. The intensities given are visual estimates from the spectrograms in the 1 to 10 scale and the following abbreviations are adopted for the description of the bands.

vsh—very sharp d—diffuse
sh—sharp vd—very diffuse
msh—medium sharp

RESULTS AND DISCUSSION

The fluorescence spectra of the uranyl acetate, nitrate, sulphate, chloride, fluoride I, potassium sulphate and ammonium sulphate at liquid air and room temperatures with different exposure times are reproduced in Figs. 1 to 7, Plates IV and V. At room temperature, new bands which are diffuse, are recorded in the region of absorption corresponding to the upper state fundamental of the symmetric streching frequency of the uranyl ion. At liquid air temperature a few additional bands extending the previous data, are also recorded in the case of uranyl acetate, nitrate and sulphate.

The bands, in general, form into about seven or eight groups separated by about 860 cm^{-1} corresponding to the symmetric streching frequency of the UO_2 ion in the ground state. In all the spectra except that of fluoride I, we find the strong doublet pattern of bands repeating at regular intervals with the long wavelength member of each pair weaker than the shorter wavelength component. In the case of fluoride I a strong triplet pattern of bands repeats at regular intervals. In between the groups, a number of weaker bands are observed.

Earlier analyses :

Pant (1945) studied the fluorescence spectra of uranyl acetate, sulphate, chloride, fluoride I, fluoride II and potassium uranyl sulphate and analysed the bands of each spectrum on the basis of two electronic transitions with two close lying ground states and a common upper state. Freymann and co-workers (1946, 1947) published another analysis of the fluorescence bands of uranyl acetate, nitrate, chloride and fluoride II. They interpreted the bands on the basis of a forbidden transition with a very weak or totally absent band as (0,0) (Pant's A_0 band). The defects of both these two types of analyses have been discussed at length in our earlier paper (Rao and Narasimham, 1956).

Present analysis

The fluorescence bands of each substance have been analysed on the basis of a single electronic allowed transition (Table I to VII). The important features in the analysis of each compound are given below.

Uranyl acetate

The (0,0) band in the fluorescence spectrum of the acetate is fixed at 20587 cm^{-1}. The reasons for this choice are

(i) This band is strong both in fluorescence and absorption.

(ii) In fluorescence, this is the first strong band on the short wavelength side.

(iii) At room temperature, a fluorescence band is obtained at 21288 cm^{-1}, with a shift of 701 cm^{-1} from this band alone and the frequency corresponds to the upper state fundamental of the symmetric streching vibration of the uranyl ion, recorded in absorption.

(iv) In absorption experiments, two pairs of emission bands have been recorded on the long wavelength side of the (0,0) band agreeing with the first two strong pairs of fluorescence bands. These emission bands could be interpreted as $0\text{-}n\times 860$ and $0\text{-}940\text{-}n\times 860$ with the (0,0) band at 20587 cm^{-1} (Narasimham and Rao, 1960).

Out of the 57 bands in acetate, about 46 bands could be interpreted on the basis of four fundamentals in the ground state 860 (U—0 symmetric streching), 940 (U—0 asymmetric streching), 222 (0—U—0 symmetric bending) and 36 cm^{-1} (crystal lattice vibration) and three frequencies in the upper state 701, 210 and 33 cm^{-1} (see Table I). The band at 19968 cm^{-1} is taken as due to the fundamental 599 characteristic of the acetate radical. This suggestion is only a possibility adopted from Dieke's (1949) observation that, in acetates, a fundamental of about 600 cm^{-1} is generally observed.

Uranyl nitrate

For the same reasons as in acetate, the strong band at 20582 cm^{-1} has been

chosen as the (0,0) band. Out of a total 60 bands, 51 bands could be interpreted on the basis of four fundamentals in the ground state 866 cm^{-1} (U—O symmetric streching), 949 cm^{-1} (U—O asymmetric streching) 222 cm^{-1} (symmetric bending) and 31 cm^{-1} (crystal lattice frequency) and three fundamentals in the upper state 722 cm^{-1} (corresponding to 860 cm^{-1} in the ground state), 210 and 33 cm^{-1} (Table II). The band at 20028 cm^{-1} is interpreted as due to a fundamental 554 cm^{-1}. Two more such bands are observed in the next groups. A possible suggestions is that this may be a fundamental of the nitrate radical.

Uranyl sulphate

The fixing up of the (0, 0) band in the sulphate spectrum is a problem of special interest. At liquid air temperature the first prominent band in fluorescence is at 20316 cm^{-1} .

TABLE I

Fluorescence bands of uranyl acetate

Wave-number of the band cm^{-1}	Inton-sity	Shift from (0,0) band ($\Delta\nu$)	Assignment		
			Present author	Freymann (1947)	Pant (1945)
(1)	(2)	(3)	(4)	(5)	(6)
21288**	2 vd	+ 701	0+701=701		
20739*?	1 d	+ 152		(0,0)	A_o
20620*	1 msh	+ 33	0+33=33		
20587*	8 sh		(0,0)	0+720−860	B_o
20551	3 msh	− 36	0−36=36		
20463	2 sh	− 124			
20426	3 sh	− 161		0+2×720−2×860	D_o
20365	2 sh	− 222	0−222=222	0+720−860−210	B_o−235
20270	2 sh	− 317		0+720−930−210	A_o−2×235
20146	3 sh	− 441	0−2×222=444	0+720−860−2×210	B_o−2×235
20112	2 sh	− 475	0−36−2×222=480		
20059	1 sh	− 528			
19988	1 sh	− 599	0−599=599		
19874	2 sh	− 713	0+210−940=730	0−860	A_o−855
19808	1 msh	− 778			
19763	2 msh	− 824	0+33−860=827		
19727***	10 sh	− 860	0−860=860	0+720−2×860	B_o−855
19683	3 d	− 904	0−36−860=896		
19647***	6 sh	− 940	0−940=940	0+720−860−930	A_o−855−235
19618	2 d	− 969	0−36−940=976		
19556	3 sh	−1031		0+720−2×930 or 0+2×720−3×860	D_o−855
19509	3 sh	−1078	0−222−860=1082	0+720−2×860−210	B_o−855−235
19461	3 sh	−1126	0−36−222−860=1118		
19411	3 sh	−1176		0+720−860−930 −210	A_o−855−2×235
19366	1 d	−1221			B_o−855−2×235

TABLE I (Contd.)

Wave-number of the band cm^{-1}	Intensity	Shift from (0,0) band ($\Delta\nu$)	Assignment		
			Present author	Freymann (1947)	Pant (1945)
(1)	(2)	(3)	(4)	(5)	(6)
19312	2 d	−1275	$0-2\times222-860=1304$		
19255	2 d	−1332			
19168	1 msh	−1419			
19107	2 msh	−1480	$0-599-860=1459$		
19020	2 sh	−1567	$0+210-940-860=1590$	$0-2\times860$	$A_0-2\times855$
18898	1 d	−1689	$0+33-2\times860=1687$		
18866***	10 sh	−1721	$0-2\times860=1720$	$0+720-3\times860$	$B_0-2\times855$
18789***	8 sh	−1798	$0-940-860=1800$	$0+720-2\times860-930$	$A_0-2\times855-235$
18746	2 msh	−1841	$0-36-940-860=1836$		
18705	2 sh	1882		$0+720-860-2\times930$ or $0+2\times720-2\times860$	$D_0-2\times855$
18664	2 sh	−1923	$0-222-2\times860=1942$	$0+720-3\times860$	
18608	2 sh	−1979			$B_0-2\times855-235$
18552	2 sh	−2035		$0+720-2\times860-930-210$	$A_0-2\times855-2\times235$
18412	1 d	−2175	$0-2\times222-2\times860=2164$		
18153	1 msh	−2434	$0+210-940-2\times860=2450$	$0-3\times860$	$A_0-3\times855$
18009	8 sh	−2578	$0-3\times860=2580$	$0+720-4\times860$	$B_0-3\times855$
17982	2 msh	−2605	$0-36-3\times860=2616$		
17926	6 sh	−2661	$0-940-2\times860=2660$	$0+720-3\times860-930$	$A_0-3\times855-235$
17895	1 d	−2692	$0-36-940-2\times860=2696$		
17802	2 d	−2785			
17771	1 msh	−2816	$0-222-3\times860=2802$		$B_0-3\times855-235$
17678	1 d	−2909		$0+720-3\times860-930-210$	$A_0-3\times855-2\times235$
17147	6 sh	−3440	$0-4\times860=3440$	$0+720-5\times860$	
17072	4 sh	−3515	$0-940-3\times860=3520$	$0+720-4\times860-930$	
17053	1 msh	−3534	$0-36-940-3\times860=3556$		
17005	2 d	−3582			
16482	1 d	−4105			
16303	1 d	−4284			
16273	3 sh	−4314	$0-5\times860=4300$	$0+720-6\times860$	
16205	2 sh	−4382	$0-940-4\times860=4380$	$0+720-5\times860-930$	
16091	1 msh	−4496	$0-222-5\times860=4522$		
15439	2 sh	−5148	$0-6\times860=5160$		
15392	2 sh	−5195	$0-940-5\times860=5240$		

* These bands are recorded in absorption also.

** This band is obtained at room temperature.

*** These bands are obtained in absorption as emission bands.

TABLE II

Fluorescence bands of uranyl nitrate

Wave number of the band cm^{-1}	Intonsity	Shift from (0,0) band	Assignment	
			Present author	Freymann (1947)
(1)	(2)	(3)	(4)	(5)
22001**	1 vd	+ 1419	0 + 2×722 = 1444	
21304**	2 vd	+ 722	0 + 722 = 722	
20618*	1 d	+ 36	0+36=36	
20582*	8 sh		(0,0)	0 + 720−860
20551	3 msh	− 31	0−31=31	
20523	1 d	− 59	0−2×31=62	
20440	3 msh	− 142		
20392	2 sh	− 190	0 + 36−222=186	0 + 720 − 860−230
20360	2 sh	− 222	0−222=222	
20114	2 msh	− 468	0−2×222 = 444	
20028	1 msh	− 554	0−554=554	
19924	3 sh	− 658	0 + 210−866=656	0+720−860−3×230
19887	3 sh	− 695	0−31 + 210−866 = 687	
19823	2 d	− 759	0 + 210 − 949=739	0 − 930
19762	2 d	− 820	0+36−866 = 830	
19716***	10 sh	− 866	0 − 866=866	0 + 720−2×860
19683	3 d	− 899	0−31 − 866=897	
19633***	6 sh	− 949	0−949 = 949	0 + 720−860 − 930 or 0 − 860−230
19588	2 d	− 994	0−31−949=980	
19545	2 msh	−1037		0 + 720−2×860−930 or 0−930−230
19505	3 sh	−1077	0 − 222−866 = 1088	
19455	3 sh	−1127	0−31 − 222−866 = 1119	0 + 720−860−930−230
19316	2 d	−1266	0−2×222 − 866 = 1310	0 + 720 − 2×860−2×230
19225	2 d	−1357		0 + 720−860− 930−2×230
19160	1 d	−1422	0−554−866=1420	
19057	3 msh	−1525	0 + 210−2×866 = 1522	0 + 720−2×860−3×230
18965	2 msh	−1617	0 + 210−949−866 = 1605	0 − 860−930
18854***	8 sh	−1728	0−2×866=1732	0 + 720− 3×860
18827	2 d	−1755	0−31−2×866=1763	
18777***	8 sh	−1805	0−949−866=1815	0 + 720−2×860−930 or 0−2×860−230
18738	2 d	−1844	0−31−949−866 = 1846	
18688	2 msh	−1894		0 + 720 − 3×860−230 or 0 − 860 − 930−230
18635	2 sh	−1947	0−222−2×866=1954	0 + 720−2×860−930−230
18593	2 msh	−1989	0−31−222−2×866 = 1984	
18562	1 msh	−2020		
18530	1 msh	−2052		
18494	1 d	−2088		0 + 720−3×860−2×230
18412	2 d	−2170	0−2×222−2×866=2176	
18185	1 d	−2397	0+210−3×866=2388	
18105	1 d	−2477		0−2×860−930

TABLE II (contd)

Wave number of the band cm^{-1}	Intensity	Shift from (0,0) band	Assignment	
			Present author	Freymann (1947)
(1)	(2)	(3)	(4)	(5)
17984	6 sh	−2598	0−3×866−2598	0 + 720−4×860
17916	6 sh	−2666	0−949−2×866=2681	0 + 720 −3×860−930 or 0−3×860−230
17803	2 d	2779		
17770	2 msh	−2812	0− 222−3×866−2820	0+720−3×860−930−230
17726	2 msh	−2856	0−31 −222− 3×866=2850	
17501	2 d	−3081	0− 2×222− 3×866=3042	0 + 720− 3×860−930 −2×230
17458	1 d	−3124	0−554 −3×866= 3152	
17199	1 d	−3383	0+210−949−3×866−3337	
17137	4 sh	−3445	0−4×866=3464	0 + 720−5×860
17042	4 sh	−3540	0−949 3×866−3547	0+720−4×860 −930 or 0− 4×720−230
17011	2 msh	−3571	0 −31− 949−3×866 − 3578	0+720−5×860 230 or 0−3×860− 930−230
16898	2 msh	−3684	0−222 −4×866 −3686	0 + 720− 4×860− 930−230
16629	2 d	−3953	0− 2×222−4 × 866 3908	0 + 720−860− 930 +2×230
16267	3 sh	−4315	0− 5×866 =4330	0 + 720− 6×860
16193	3 sh	−4389	0− 949−4×866=4413	0 + 720 − 5×860 930 or 0− 5×860−230
16045	2 msh	−4537	0−222−5×866 4552	
15900	1 d	−4682		
15780	1 d	−4802	0−2×222 −5×866 4774	
15438	2 msh	−5144	0−6×866−5196	0 + 720− 7×860
15362	2 d	−5220	0− 949−5×866= 5279	0−6×869−230

* These bands are recorded in absorption also.

** These bands are observed at room temperature.

*** These bands are recorded in absorption as emission bands.

However, at the same temperature but with longer exposures, a less prominent band develops at 20560 cm^{-1}. The frequency shift between these two is 244 cm^{-1}. The values for these bands in absorption are 20317 and 20561 cm^{-1} respectively. But the band at 20561 cm^{-1} is much stronger than that at 20317 cm^{-1}. It is possible to understand this intensity variation if we assume the (0, 0) band to be at 20560 cm^{-1} and interpret the 20316 cm^{-1} as 0—244 (ν_2 bending frequency). In the fluorescence spectra of many organic molecules the (0, 0) band is extremely weak compared with some of the fundamentals due to the phenomenon of self-absorption. A similar process may be considered as responsible for the weakness of this (0, 0) band in fluorescence (20560 cm^{-1}).

The analysis of the sulphate spectrum (Table III) presents some unique features. The actual fundamentals are 857, 931, 244 and 25 cm^{-1} in the ground state of the uranyl ion and 729, 242 and 32 cm^{-1} in the upper state. In the

acetate and nitrate spectra, the frequency 222 cm^{-1} represented by a weak band whereas in the sulphate, this frequency 244 cm^{-1} has a high intensity. All strong bands of the spectrum could be interpreted only in terms of combination with this fundamental. It is clear that this fundamental 244 plays an important role in the fluorescence spectrum. Another fundamental 962 cm^{-1} is assigned as a possible sulphate ion frequency.

Sevchenko and Stepanov (1949) studied the infra red absorption of the sulphate and observed frequencies forbidden for a linear model of the uranyl ion. Therefore, they concluded that the uranyl ion is bent in sulphate. The fact that the bending frequency 244 cm^{-1} is very strong in the fluorescence spectrum of the sulphate is a further justification for the idea that the uranyl ion is bent in sulphate.

TABLE III

Fluorescence bands of uranyl sulphate

Wave number of the band cm^{-1}	Intensity	Shift from (0,0) band cm^{-1} obs. value	Assignment
(1)	(2)	(3)	(4)
21289**	2 vd	+ 729	0 + 729 = 729
21066**	1 vd	+ 506	
20560*	1 sh		(0,0)
20442*	1 sh	− 118	
20379*	2 sh	− 181	0 + 2 × 32 − 244 − 180
20348*	2 sh	− 212	0 + 32 − 244 − 212
20316*	7 vsh	− 244	0 − 244 − 244
20291	3 vsh	− 269	0 − 25 − 244 − 269
20262	2 sh	− 298	0 − 25 − 244 − 294
20228	1 sh	− 332	
20177	3 sh.	− 383	
20149	3 sh	− 411	
20124	1 sh	− 436	
20095	1 msh	− 465	0 + 32 − 2 × 244 − 456
20065***	3 sh	− 495	0 − 2 × 244 − 488
20040	2 msh	− 520	0 − 25 − 2 × 244 − 513
19987	1 msh	− 573	0 + 32 + 242 − 857 − 583
19949	2 sh	− 611	0 + 242 − 257 − 615
19929	1 msh	− 631	0 − 25 + 242 − 857 = 640
19890	2 msh	− 670	
19864	1 msh	− 696	
19810	2 sh	− 750	0 − 3 × 244 = 732
19776	1 msh	− 784	
19703***	6 vsh	− 857	0 − 857 = 857
19629	2 sh	− 931	0 − 931 = 931
19598	1 msh	− 962	0 − 962 = 962
19560	1 msh	−1000	
19521	3 msh	−1039	0 + 2 × 32 − 244 − 857 = 1037
19498	4 msh	−1062	0 + 32 − 244 − 857 = 1069
19464***	10 vsh	−1096	0 − 244 − 857 = 1101

TABLE III (contd.)

Wave number of the band cm^{-1}	Intensity	Shift from (0,0) band cm^{-1} obs. value	Assignment
(1)	(2)	(3)	(4)
19430	2 sh	− 1130	0 − 25 − 244 − 857 = 1126
19392	1 sh	− 1168	0 − 2 × 25 − 931 − 244 = 1151
19372***	6 vsh	− 1188	0 − 931 − 244 = 1175
19337	1 msh	− 1223	
19316	2 sh	− 1244	
19259	1 msh	− 1301	
19216	2 sh	− 1344	0 − 2 × 244 − 857 = 1345
19195	2 msh	− 1365	0 − 25 − 2 × 244 − 857 = 1370
19111	1 msh	− 1449	0 + 242 − 2 × 857 = 1472
19009	2 msh	− 1551	0 − 3 × 244 − 857 = 1589
18910	1 msh	− 1650	
18858	6 sh	− 1702	0 − 2 × 857 = 1714
18787	1 msh	− 1773	0 − 962 − 857 = 1819
18609***	10 vsh	− 1951	0 − 244 − 2 × 857 = 1958
18574	2 sh	− 1986	0 − 25 − 244 − 2 × 857 = 1983
18528***	8 vsh	− 2032	0 − 931 − 244 − 857 = 2032
18465	2 msh	− 2095	
18337	2 msh	− 2223	0 + 2 × 244 − 2 × 857 = 2202
18243	2 msh	− 2317	0 + 242 − 3 × 857 = 2329
18207	2 msh	− 2353	
17992	4 vsh	− 2567	0 − 3 × 857 = 2571
17924	1 d	− 2636	0 − 962 − 3 × 857 − 2676
17759	8 vsh	− 2801	0 − 244 − 3 × 857 = 2815
17671	6 vsh	− 2889	0 − 931 − 244 − 2 × 857 = 2889
17576	2 msh	− 2984	
17490	1 d	− 3070	0 − 2 × 244 − 3 × 857 = 3059
17186	1 d	− 3374	
17141	2 sh	− 3419	0 − 4 × 857 = 3428
17024	1 sh	− 3536	0 − 962 − 3 × 857 = 3533
16896	6 vsh	− 3664	0 − 244 − 4 × 857 = 3672
16806	6 vsh	− 3754	0 − 931 − 244 − 3 × 857 = 3746
16720	2 sh	− 3840	
16613	1 msh	− 3947	0 − 2 × 244 − 4 × 857 = 3916
16535	1 msh	− 4025	0 + 242 − 5 × 857 = 4041
16378	1 d	− 4182	
16171	1 msh	− 4389	0 − 962 − 4 × 857 = 4390
16119	1 msh	− 4441	
16061	2 sh	− 4499	0 − 244 − 5 × 857 = 4529
15980	2 sh	− 4580	0 − 931 − 244 − 4 × 857 = 4603
15908	1 msh	− 4652	
15210?	1 d	− 5350	0 − 244 − 6 × 857 = 5386
15136?	1 d	− 5424	0 − 931 − 244 − 5 × 857 = 5460

* These bands are recorded in absorption also.

** These bands are obtained at room temperature.

*** These bands are recorded in absorption as emission bands.

Uranyl fluoride—I :

Out of the three fluorides i.e., anhydrous fluoride and two hydrated varieties called by Pant (1945) as fluoride I and fluoride II, fluoride I is the only compound which has shown fluorescence. The triplet pattern of bands observed in the fluorescence spectrum of fluoride I immediately makes us suspect whether this spectrum is entirely due to fluoride I or possibly due to any other fluoride that may exist as an inpurity in fluoride I. On a comparison of the two bands at 20012 and 20092 cm^{-1} with those two observed in absorption of fluoride I and fluoride II, it was noted that the band at 20092 cm^{-1} in fluorescence can be attributed to fluoride II while the stronger band at 20012 cm^{-1} can be attributed to fluoride I. If we take these two as the (0, 0) bands for the two fluorides, all the bands could be explained on the basis of two series: Series I consisting of the comparatively weaker bands made out of the short-wavelength components of the triplet structure to be attributed to fluoride II and series II consisting of the central strong bands and the long wave length components of the triplet structures making the usual doublet patterns obtained in all other fluorescence spectra and interpreted on the same lines. This classification is indicated in fig. 4, Plate IV (B) and Table IV.

The shift between the two (0, 0) bands of the two fluorides is 80 cm^{-1}. The values of the symmetric streching fundamental (ν_1) in fluoride I and fluoride II are respectively 824 and 814 cm^{-1} while the value of the asymmetric streching frequency (ν_3) in fluoride I is 891 cm^{-1}. The ν_3 frequency of fluoride II may have about 70 cm^{-1} shift from the ν_1 and it makes its ν_3 fundamental and its combinations with the ν_1 fall on the ν_1 fundamental and its overtones of flouride I. This might account for the singlet structure of the bands attributed to flouride II.

TABLE IV

Fluorescence bands of uranyl fluoride I and II

Wave-number of the band cm^{-1}	Intensity	Shift from (0,0) F. I	Shift from (0,0) F. II	Assignment: Present author, Fluoride I	Assignment: Present author, Fluoride II	Pant (1945)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
20687*	1 vd	+ 675	+ 595	0+675=675		
20092**	4 vsh	+ 80			(0,0)	B_o
20070**	1 msh	+ 58	− 22			
20012**	7 vsh		− 80	(0,0)		A_o-176
19980	1 msh	− 32	− 112	0−32=32		D_o
19918	1 msh	− 94	− 174			B_o-176
19894	2 msh	− 118	− 198		0−198=198	
19812	1 msh	− 200	− 280	0−200=200		D_o-176
19591	2 msh	− 421	− 501	0−2×200=400		$B_o-3\times176$
19489	1 msh	− 523	− 603			

TABLE IV—(contd).

Wave-number of the band cm^{-1}	Intensity	Shift from (0,0) F. I	Shift from (0,0) F. II	Assignment — Present author Fluoride I	Assignment — Present author Fluoride II	Assignment — Pant (1945)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
19453	1 msh	− 559	− 639			
19278***	6 vsh	− 734	− 814		0−814 = 814	B_0 − 819
19188***	10 vsh	− 824	− 904	0−824 = 824		A_0 − 827 − 176
19121***	7 vsh	− 891	− 971	0−891 = 891		B_0 − 819 − 176
19085	1 msh	− 927	−1007		0−198−814 = 1012	
18911	2 sh	−1101	−1181	0−200−891 = 1091		A_0 − 827 − 2×176
18810	3 sh	−1202	−1282	0−2×200−824 = 1224		A_0 − 827 − 3×176
18763	2 msh	−1249	−1329			
18726	1 msh	−1286	−1366			B_0 − 819 − 3×176
18639	3 sh	−1373	−1453			
18574	1 msh	−1438	−1518	0−3×200−824 = 1424		
18542	1 d	−1470	−1550			
18502	1 d	−1510	−1590			A_0 − 2×827
18463***	5 vsh	−1549	−1629		0−2×814 = 1628	B_0 − 2×819
18405	2 sh	−1607	−1687			D_0 − 2×795
18363***	8 sh	−1649	−1729	0−2×824 = 1648		A_0 − 2×827 − 176
18295***	6 sh	−1717	−1797	0−891−824 = 1715		B_0 − 2×819 − 176
18154	1 msh	−1858	−1938	0−200−2×824 = 1848		B_0 − 2×795 − 176
18125	1 msh	−1887	−1967			
18082	1 sh	−1930	−2010	0−200−891−824 = 1915		B_0 − 2×819 − 2×176
18026	2 sh	−1986	−2066			
17934	1 d	−2078	−2158	0−2×200−2×824 = 2048		B_0 − 3×819 − 2×176
17657	3 sh	−2355	−2435		0−3×814 = 2442	B_0 − 3×819
17595	2 sh	−2417	−2497			B_0 − 3×795
17542	6 sh	−2470	−2550	0−3×824 = 2472		A_0 − 3×827 − 176
17480	4 sh	−2532	−2612	0−891−2×824 = 2539		B_0 − 3×819 − 176
17191	2 d	−2821	−2901			
17031	2 sh	−2981	−3061			
16838	2 msh	−3174	−3254		0−4×814 = 3256	
16777	2 msh	−3235	−3315			
16704	4 sh	−3308	−3388	0−4×824 = 3296		
16653	3 sh	−3359	−3439	0−891−3×824 = 3363		
15913	1 msh	−4099	−4179	0−5×824 = 4120		
15855	1 msh	−4157	−4237	0−891−4×824 = 4187		

* This band is recorded at room temperature.

** These bands are obtained in absorption also.

** These bands are obtained as emission bands in absorption experiments.

The other fundamentals obtained in the fluorescence spectrum of fluoride I are the bending frequency of 200 cm^{-1} (v_2), the crystal lattice frequency of 32 cm^{-1} in the ground state and 675 cm^{-1} of the v_1 frequency in the upper state.

TABLE V

Fluorescence bands of urnayl chloride

Wave-number of the band cm^{-1}	Inten-sity	Shift from (0,0) band	Assignment		
			Present author	Freymann (1947)	Pant (1945)
(1)	(2)	(3)	(4)	(5)	(6)
20547*	1 msh	+ 26	0+26	0 + 720 − 875	B_0
20521*	5 sh		(0,0)		
20443*	2 msh	− 78		0 + 720 − 930 or 0 − 230	A_0 − 246
20275	3 sh	− 246	0 − 246 − 246	0 + 720 − 875 − 230	B_0 − 246
20213	2 d	− 308		0 + 720 − 930 − 230	
20144	1 d	− 377			A_0 − 2 × 246
19641	10 sh	− 880	0 − 880 − 880	0 + 720 − 2 × 875	B_0 − 876
19557	10 sh	− 964	0 − 964 = 964	0 + 720 − 875 − 930 or 0 − 875 − 230	A_0 − 876 − 246
19391	5 sh	− 1130	0 − 246 − 880 − 1126	0 + 720 − 2 × 875 − 230 or 0 − 930 − 230	B_0 − 876 − 246
19327	2 d	− 1194	0 − 246 − 964 = 1210		
19248	1 d	− 1273			
18762	8 sh	− 1759	0 − 2 × 880 − 1760	0 + 720 − 3 × 875	
18681	10 sh	− 1840	0 − 964 − 880 = 1844	0 + 720 − 2 × 875 − 930 or 0 − 2 × 875 − 230	
18515	5 sh	− 2006	0 − 246 − 2 × 880 = 2006	0 + 720 − 3 × 875 − 230 or 0 − 875 − 930 − 230	
18452	1 d	− 2069	0 − 246 − 964 − 880 − 2090		
18370	1 d	− 2151			
17884	4 sh	− 2637	0 − 3 × 880 = 2640	0 + 720 − 4 × 875	
17806	8 sh	− 2715	0 − 964 − 2 × 880 = 2724	0 + 720 − 4 × 875 − 230	
17636	4 msh	− 2885	0 − 246 − 3 × 880 = 2886	0 − 2 × 875 − 930 − 230	
17551	1 d	− 2970	0 − 246 − 964 − 2 × 880 = 2970		
16989	2 sh	− 3532	0 − 4 × 880 = 3520	0 + 720 − 5 × 875	
16920	4 sh	− 3601	0 − 964 − 3 × 880 − 3604	0 + 720 + 4 × 875 − 930 or 0 − 4 × 875 − 230	
16755	1 d	− 3766	0 − 246 − 4 × 880 = 3766	0 + 720 − 5 × 875 − 230 or 0 − 3 × 875 − 930 − 230	

These bands are obtained in absorption also.

TABLE VI

Fluorescence bands potassium uranyl sulphate

Wave-number of the band cm^{-1}	Intensity	Shift from (0,0) band	Assignment	
			Present author	Pant (1945)
(1)	(2)	(3)	(4)	(5)
21035**	1 vd	+ 662	0 + 662 = 662	
20476*	1 d	+ 103	0 + 3 × 30 = 90	A_0
20431*	2 sh	+ 58	0 + 2 × 30 = 60	
20373*	10 vsh		(0,0)	B_0
20329*	2 sh	− 44	0 − 44 = 44	
20302*	4 sh	− 71	0 − 2 × 44 = 88	A_0 − 172
20263	2 sh	− 110		D_0
20241*	3 sh	− 132		
20211	3 sh	− 162		
20179	2 msh	− 194	0 − 194 = 194	B_0 − 172
20148	1 msh	225		
20094	6 sh	279	0 − 279 = 279	A_0 − 2 × 172
20046	2 sh	327	0 − 44 − 279 = 323	B_0 − 2 × 172
19956	2 sh	417	0 − 417 = 417	A_0 − 3 × 172
19895	1 msh	478		D^0 − 2 × 172
19850	1 msh	523		
19824	1 msh	549	0 − 2 × 279 558	
19776	1 msh	597	0 − 597 . 597	A_0 − 4 × 172
19706	1 sh	667		B_0 − 4 × 172
19636	2 d	737	0 + 3 × 30 − 837 = 747	A_0 − 833
19601	3 msh	772	0 + 2 × 30 − 837 = 777	
19566	5 msh	807	0 + 30 − 837 = 807	
19536***	10 vsh	837	0 − 837 = 837	B_0 − 833
19458***	7 vsh	915	0 − 915 = 915	A_0 − 833 − 172
19109	3 sh	964	0 − 44 − 915 = 959	
19372	5 vsh	1001	0 − 1001 = 1001	B_0 − 833 − 172
19346	2 d	-1027	0 − 194 − 837 = 1031	
19314	2 d	-1059		
19260	7 sh	-1113	0 − 279 − 837 = 1116	A_0 − 833 − 2 × 172
19219	2 msh	-1144	0 − 44 − 279 − 837 = 1160	B_0 − 833 − 2 × 172
19155	1 d	-1218		
19104	3 msh	-1269	0 − 417 − 837 = 1254	A_0 − 833 − 3 × 172
19063	2 msh	-1310		B_0 − 833 − 2 × 172
18936	2 msh	-1437	0 − 597 − 837 = 1434	A_0 − 833 − 4 × 172
18872	2 msh	-1501		B_0 − 833 − 4 × 172
18804	1 d	-1569		
18765	2 d	-1608	0 + 2 × 30 − 2 × 837 = 1614	
18732	5 msh	-1641	0 + 30 − 2 × 837 = 1644	
18703***	10 vsh	-1670	0 − 2 × 837 = 1674	
18626***	6 vsh	-1747	0 − 915 − 837 = 1752	
18587	1 d	-1786	0 − 44 − 915 − 837 = 1796	
18536	5 sh	-1837	0 − 1001 − 837 = 1838	
18483	1 d	-1890	0 − 194 − 2 × 837 = 1868	
18431	4 sh	-1942	0 − 279 − 2 × 837 = 1953	
18376	3 sh	-1997	0 − 44 − 279 − 2 × 837 = 1997	

TABLE VI (contd.)

Wave-number of the band cm^{-1}	Intensity	Shift from (0,0) band cm^{-1}	Assignment	
			Present author	Pant (1945)
(1)	(2)	(3)	(4)	(5)
18299	2 d	−2074	0−417−2×837=2091	
18097	1 msh	−2276	0−795−2×837=2271	
18032	1 msh	−2341		
17903	3 d	−2470	0+30−3×837=2481	
17875	8 sh	−2498	0−3×837=2511	
17797	5 sh	−2576	0−915−2×837=2589	
17744	1 d	−2629	0−44−915−2×837=2633	
17706	3 sh	−2667	0−1001−2×837=2675	
17646	1 d	−2727	0−194−3×837=2705	
17592	2 msh	−2781	0−279−3×837=2790	
17541	2 msh	−2832	0−44−279−3×837=2834	
17461	1 msh	−2912	0−417−3×837=2928	
17357	1 d	−3016		
17184	1 d	−3189		
17143	1 d	−3230		
17055	2 msh	−3318	0+30−4×837=3318	
17024	5 sh	−3349	0−4×837=3348	
16951	3 sh	−3422	0−915−3×837=3426	
16851	2 sh	−3522	0−1001−3×837=3512	
16774	1 msh	−3599	0−279−4×837=3627	
16706	1 msh	−3667	0−44−279−4×837=3671	
16583	1 msh	−3790	0−417−4×837=3675	
16482	1 d	−3891		
16202	2 sh	−4171	0−5×837=4185	
16134	1 sh	−4239	0−915−4×837=4263	
15326**	1 vd	−5047	0−6×837=5022	

* These bands are also obtained in absorption.

** These bands are recorded at room temperature only.

*** These bands are obtained as emission bands in absorption experiments.

Uranyl chloride

The first strong band in fluorescence is at 20521 cm^{-1} which is also strong in absorption (value 20530 cm^{-1}). Therefore, this band is chosen as the (0, 0) band. The other bands could be interpreted on the basis of three fundamentals in the ground state 880 cm^{-1} (symmetric streching), 964 cm^{-1} (asymmetric strech-

ing) and 246 cm^{-1} (symmetric bending) and one fundamental in the upper state 26 cm^{-1} (crystal lattice frequency) (Table V). It is seen that the 880 fundamental and its overtones are weaker in intensity than 964 fundamental and its combinations with 880 fundamental fig. 5, Plate V (A) which shows violation of selection rules due to the crystalline fields.

Potassium uranyl sulphate

The first strong band at 20373 cm^{-1} is chosen as the (0, 0) band for reasons similar to those in acetate. Most of the other bands could be explained on the basis of five fundamentals in the ground state 837 cm^{-1} (symmetric streching), 915 cm^{-1} (asymmetric streching), 194 and 279 cm^{-1} (symmetric bending) and 44 cm^{-1} (crystal lattice frequency) and two fundamentals in the upper state 662 cm^{-1} (symmetric streching) and 30 cm^{-1} (crystal lattice frequency) (Table (VI). Among the two fundamentals belonging to the bending vibration, 194 cm^{-1} corresponds to the in-plane bending frequency and 279 cm^{-1} corresponds to the out-of-plane bending frequency of the uranyl ion. These two frequencies arise due to the removal of degeneracy in the linear O--U—O ion which becomes slightly bent in the crystalline fields. The out-of-plane bending fundamental is stronger than the in-plane bending fundamental. As in sulphate, in the case of potassium uranyl sulphate also, the bands analysed as $0-279-n\times837$ appear with moderately strong intensity which shows the importance of the bending frequency. This may be taken as an indication that the uranyl ion is slightly more bent than in acetate, nitrate, etc. Sevchenko and Stepanov (1949) who studied the infra red absorption of this substance have come to the conclusion that the ion is slightly bent as some bands forbidden for a linear model of the uranyl ion are present in the spectrum.

Three possible fundamentals 417, 597, and 1001 cm^{-1} of the sulphate ion have been used in the analysis to explain some of the weak bands. These frequency values agree well with the Raman values given for the sulphate ion in sulphuric acid (Hibben, 1939).

Ammonium uranyl sulphate

The first strong band at 20348 cm^{-1} has been chosen as the (0, 0) band for the same reasons as in acetate etc. About 45 bands have been analysed on the basis of the five fundamentals in the ground state 848 cm^{-1} (symmetric streching), 926 (asymmetric streching), 207 cm^{-1} (in-plane bending) frequency, 273 cm^{-1} (out-of-plane bending frequency) and 29 cm^{-1} (crystal lattice frequency) and two fundamentals in the upper state 697 and 24 cm^{-1} (Table VII). As in the case of potassium uranyl sulphate, the two frequencies 207 and 273 cm^{-1} arise due to the removal of degeneracy in the linear O-U-O ion, which becomes slightly bent in the crystal line fields. Three possible fundamentals 473, 626, and 1195 cm^{-1}

TABLE VII

Fluorescence bands of ammonium uranyl sulphate

Wave-number of the band cm^{-1}	Inten-sity	Shift from (0,0) band cm^{-1}	Assignment
(1)	(2)	(3)	(4)
21045*	1 vd	+ 697	0 + 697 = 697
20410**	1 d	+ 62	0 + 2 × 24 = 48
20372	3 d	+ 24	0 + 24 = 24
20348**	7 sh		(0,0)
20319	4 d	— 29	0 — 29 29
20248	4 d	— 100	
20171	1 d	— 177	0 + 24 207 = 183
20141	2 msh	— 207	0 — 207 = 207
20075	3 sh	— 273	0 — 273 — 273
19995	1 msh	— 353	
19931	1 msh	— 417	0 — 2 × 207 = 414
19875	2 sh	— 473	0 — 473 = 473
19722	1 sh	— 626	0 = 626 = 626
19695	1 d	— 653	0 — 29 626 — 655
19563	2 d	— 785	0 + 2 × 24 = 484 = 800
19529	4 d	— 819	0 + 24 — 848 = 824
19500***	10 sh	— 848	0 — 848 = 848
19422***	8 sh	— 926	0 — 926 926
19311	4 d	— 1037	0 — 207 — 848 = 1055
19225	4 d	— 1123	0 — 278 — 848 = 1121
19153	2 msh	— 1195	0 — 1195 = 1195
19092	1 msh	— 1256	0 2 × 207 — 848 = 1262
19031	3 sh	— 1317	0 — 473 = 848 = 1321
18967	1 msh	— 1381	
18878	2 sh	— 1470	0 — 626 — 848 = 1474
18718	1 d	— 1630	0 + 2 × 24 = 848 — 1648
18687	2 d	— 1661	0 + 24 = 2 × 848 = 1672
18666***	10 sh	— 1682	0 — 2 × 848 = 1696
18583***	8 sh	— 1765	0 — 926 848 1774
18468	4 d	— 1880	0 — 207 — 2 × 848 = 1903
18378	4 d	— 1970	0 = 273 — 2 × 848 — 1969
18307	1 d	— 2041	0 1195 — 848 = 2043
18187	2 sh	— 2162	0 — 473 — 2 × 848 = 2169
18120	1 msh	— 2228	
18036	2 sh	— 2312	0 — 626 — 2 × 848 = 2322
17842	1 d	— 2506	
17830	8 sh	— 2518	0 = 3 × 848 = 2544
17750	6 sh	— 2598	0 — 926 — 2 × 848 = 2622
17642	3 d	— 2706	0 — 207 — 3 × 848 = 2751
17537	3 d	— 2811	0 — 273 — 3 × 848 = 2817
17556	2 msh	— 2891	0 — 1195 — 2 × 848 = 2891
17378	1 msh	— 2970	0 — 2 × 207 — 3 × 848 = 2958
17361	1 d	— 2987	0 — 473 = 3 × 848 = 3017
17192	1 d	— 3156	0 — 726 — 3 × 848 = 3170

TABLE VII (*contd.*)

Wave-number of the band cm^{-1}	Intensity	Shift from (0,0) band cm^{-1}	Assignment
(1)	(2)	(3)	(4)
16959	6 sh	−3389	$0-4\times848=3392$
16878	4 sh	− 3470	$0-926-3\times848=3470$
16791	2 sh	−3557	$0-207-4\times848=3599$
16686	1 msh	−3662	$0-273-4\times848=3655$
16147	2 sh	−4201	$0-5\times848=4240$
16073	2 sh	−4275	$0-926-4\times848=4318$
16016	1 d	−4332	

* This band is recorded at room temperature only.

** These bands are obtained in absorption also.

*** These bands are obtained as omission bands in absorption experiments.

of the sulphate ion are also identified and used in the analysis to explain some weak bands in between the groups. These frequency values are found to agree well with the Raman values given for the sulphate ion in sulphuric acid (Hibben, 1939).

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